

VERIFICATION OF TRANSLATION

Re: JAPANESE PATENT APPLICATION NO. 2004-49826

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hereby declare that I am the translator of the  
document attached and certify that the following is  
true translation to the best of my knowledge and  
belief.

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[Document Name] Claims

[Claim 1]

A photocurable resin composition for an optical waveguide, the composition comprising, as an essential component, a carboxy-  
5 containing unsaturated polyurethane resin (A) obtained by reacting a polyisocyanate compound (a), a carboxy-containing polyol (b), a hydroxy-containing unsaturated compound (c), and optionally a polyol (d).

[Claim 2]

10 The photocurable resin composition according to claim 1, wherein the polyisocyanate compound (a) is a polyisocyanate compound containing an aromatic ring in its molecule.

[Claim 3]

The photocurable resin composition according to claim 1, wherein  
15 the hydroxy-containing unsaturated compound (c) is an unsaturated compound (c-1) having one hydroxy group and one unsaturated group per molecule.

[Claim 4]

The photocurable resin composition according to claim 1, wherein  
20 the hydroxy-containing unsaturated compound (c) is an unsaturated compound (c-2) having one hydroxy group and at least two unsaturated groups per molecule.

[Claim 5]

The photocurable resin composition according to claim 1, wherein  
25 the hydroxy-containing unsaturated compound (c) is an unsaturated compound (c-3) having at least two hydroxy groups and one unsaturated group per molecule.

[Claim 6]

The photocurable resin composition according to claim 1, wherein  
30 the hydroxy-containing unsaturated compound (c) is an unsaturated compound (c-4) having at least two hydroxy groups and at least two unsaturated groups per molecule.

[Claim 7]

The photocurable resin composition according to claim 1, wherein  
35 the polyol (d) is a polyol containing an aromatic ring in its

molecule.

[Claim 8]

A photocurable dry film for forming an optical waveguide, which is formed using the photocurable resin composition according to  
5 any one of claims 1 to 7.

[Claim 9]

The photocurable dry film according to claim 8, which has a softening temperature within a range of 0°C to 300°C.

[Claim 10]

10 An optical waveguide comprising a lower cladding layer (A) , a core layer (B) and an upper cladding layer (C), wherein at least one of these layers is formed using the photocurable resin composition according to any one of claims 1 to 7 or the dry film according to claim 8 or 9.

[Document Name] Specification

[Title of the Invention] Photocurable Resin Composition for Optical Waveguide, Photocurable Dry Film for Forming Optical Waveguide, and Optical Waveguide

5 [Technical Field]

[0001]

The present invention relates to a photocurable resin composition and curable dry film suitable for optical waveguides, and an optical waveguide formed using the composition or dry film.

10 [Background Art]

[0002]

In recent years, optical waveguides have been attracting attention as optical transmission media that meet the demand for increased capacity and speed of information processing in optical communication systems, computers, etc. Quartz waveguides are representative optical waveguides, but have problems in that they require special production facilities, long production times, etc.

As substitutes for such quartz waveguides, organic polymer optical waveguides, which are unlikely to have the above problems, have been attracting attention recently. As such an organic polymer optical waveguide, Patent Document 1 disclosed an optical waveguide obtained by applying a liquid resin composition for an optical waveguide, comprising an ethylenically unsaturated group-containing carboxylic acid resin (A) having at least one ethylenically unsaturated group and at least one carboxy group per molecule, a diluent (B), and a photopolymerization initiator (C); forming a coating; and irradiating the coating with light.

[0003]

30 [Patent Document 1] Japanese Unexamined Patent Publication No. 2003-149475

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0004]

35 In the resin composition for an optical waveguide

disclosed in Patent Document 1, the ethylenically unsaturated group-containing carboxylic acid is substantially produced using a reaction product a polybasic acid anhydride with a reaction product of an epoxy resin having at least two epoxy groups per molecule with (meth)acrylic acid, optionally together with a compound having one carboxy group and two hydroxy groups per molecule. The reaction product has the problems in that the production process is complicated, that unsaturated groups and carboxy groups are not sufficiently introduced into the molecule, and that the resulting optical waveguide has poor processability, poor physical properties, etc. Furthermore, since the optical waveguide formed from the resin composition has poor processability, poor mechanical properties, etc. as mentioned above, the resin composition is not suitable especially as a dry film.

[0005]

An object of the present invention is to provide a photocurable resin composition for an optical waveguide and a photocurable dry film for an optical waveguide that have properties necessary for optical waveguides; and an optical waveguide obtained using the resin composition and/or the dry film.

[Means for solving the Problems]

[0006]

The photocurable resin composition for an optical waveguide according to the present invention comprises, as an essential component, a carboxy-containing unsaturated polyurethane resin (A) obtained by reacting a polyisocyanate compound (a), a carboxy-containing polyol (b), a hydroxy-containing unsaturated compound (c), and optionally a polyol (d).

[0007]

In a photocurable resin composition for an optical waveguide according to the present invention, the polyisocyanate compound (a) is a polyisocyanate compound containing an aromatic ring in its molecule.

[0008]

In the photocurable resin composition according to the present invention, the hydroxy-containing unsaturated compound (c) is preferably at least one member selected from an  
5 unsaturated compound (c-1) having one hydroxy group and one unsaturated group per molecule, an unsaturated compound (c-2) having one hydroxy group and at least two unsaturated groups per molecule, an unsaturated compound (c-3) having at least two hydroxy groups and one unsaturated group per molecule, and an  
10 unsaturated compound (c-4) having at least two hydroxy groups and at least two unsaturated groups per molecule.

[0009]

In a photocurable resin composition according to the present invention, the polyol (d) is a polyol containing an  
15 aromatic ring in its molecule.

[0010]

The photocurable dry film for forming an optical waveguide according to the present invention is formed using the photocurable resin composition according to the present invention.  
20

[0011]

A photocurable dry film according to the present invention has a softening temperature within a range of 0°C to 300°C.

[0012]

The optical waveguide according to the present invention comprises a lower cladding layer (A), a core layer (B) and an upper cladding layer (C), wherein at least one of these layers is formed using the photocurable resin composition according to the present invention or the dry film according to  
30 the present invention.

[Effects of the Invention]

[0013]

The carboxy-containing unsaturated polyurethane resin (A) forming the photocurable resin composition of the present  
35 invention can be easily produced by reacting a polyisocyanate

compound, a carboxy-containing polyol, and a hydroxy-containing unsaturated compound. The high reactivity between isocyanate groups and hydroxy groups ensures the introduction of unsaturated groups and carboxy groups into the resin. Since a resin having a urethane bond can be obtained by the reaction of isocyanate groups with hydroxy groups, the resin composition has excellent processability, excellent mechanical properties, etc. and thus is especially suitable for use as a dry film. The use of the polyisocyanate compound having an aromatic ring enables a high reactivity and formation of a core layer with a high refractive index.

[Best Mode for Carrying Out the Invention]

[0014]

The photocurable resin composition of the present invention comprises as an essential component a carboxy-containing unsaturated polyurethane resin (A) obtained by reacting a polyisocyanate compound (a), a carboxy-containing polyol (b), a hydroxy-containing unsaturated compound (c), and optionally a polyol (d).

[0015]

Polyisocyanate compound (a):

The polyisocyanate compound is used to bond the compound that introduces a carboxy group into the molecule, to the compound that introduces a photopolymerizable unsaturated group at a molecular end.

Polyisocyanate compounds include, for example, aliphatic diisocyanates, aromatic diisocyanates, alicyclic diisocyanates and other polyisocyanates.

[0016]

Examples of aliphatic diisocyanates include hexamethylene diisocyanate, trimethylene diisocyanate, 1,4-tetramethylene diisocyanate, pentamethylene diisocyanate, 1,2-propylene diisocyanate, 1,2-butylene diisocyanate, trimethylhexamethylene diisocyanate, dimer acid diisocyanate, lysine diisocyanate, 2,3-butylene diisocyanate, 1,3-butylene

diisocyanate, etc. Examples of alicyclic diisocyanate compounds include isophorone diisocyanate, 4,4'-methylenebis(cyclohexyl isocyanate), methylcyclohexane-2,4-(or -2,6-)diisocyanate, 1,3-(or 1,4-)di(isocyanatomethyl)cyclohexane, 1,4-cyclohexane  
5 diisocyanate, 1,3-cyclopentane diisocyanate, 1,2-cyclohexane diisocyanate, etc. Examples of aromatic polyisocyanates include xylylene diisocyanate, metaxylylene diisocyanate, tetramethylxylylene diisocyanate, tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 1,5-naphthalene diisocyanate, 1,4-  
10 naphthalene diisocyanate, 4,4'-toluidine diisocyanate, 4,4'-diphenylether diisocyanate, (m- or p-)phenylene diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate, bis(4-isocyanatophenyl)sulfone, isopropylidenebis(4-phenylisocyanate), etc. Examples of other  
15 polyisocyanates include triphenylmethane-4,4',4''-triisocyanate, 1,3,5-triisocyanatobenzene, 2,4,6-triisocyanatotoluene, 4,4'-dimethyldiphenylmethane-2,2',5,5'-tetraisocyanate and like polyisocyanate compounds having at least three isocyanate groups; adducts obtained by reacting a polyisocyanate with a polyol such  
20 as ethylene glycol, propylene glycol, 1,4-butylene glycol, polyalkylene glycol, trimethylolpropane, hexane triol or the like, in such a ratio that the isocyanate groups are present in excess relative to the hydroxy groups of the polyol; biuret-type adducts or isocyanuric ring-type adducts of hexamethylene diisocyanate,  
25 isophorone diisocyanate, tolylene diisocyanate, xylylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 4,4'-methylenebis(cyclohexyl isocyanate), etc.; and the like. These can be used singly or in combination.

Among the compounds mentioned above, aromatic  
30 diisocyanate compounds hardly undergo alkaline hydrolysis and thus are capable of forming photocurable layers with high resistance to alkaline developers, and are capable of forming optical waveguides made of tough coating films. Aromatic diisocyanates are especially preferable also because  
35 they can form core layers with high refractive indices.



[0017]

Carboxy-containing polyol (b):

The carboxy-containing polyol (b) introduces carboxy groups into the molecule to make it possible to obtain an aqueous dispersion of a photopolymerizable composition, and to remove the unirradiated portion of a coating film by alkaline development treatment.

[0018]

Compounds usable as the carboxy-containing polyol (b) include those having at least one carboxy group and at least two hydroxy groups per molecule. Specific examples include 2,2-dimethylolpropionic acid, 2,2-dimethylolacetic acid, 2,2-dimethylolpentanoic acid, half ester compounds obtained by reacting triol compounds with acid anhydride compounds, sulfonate diol compounds obtained by transesterification of sodium dimethyl sulfoisophthalate with an excess of glycol, etc. Such compounds can be used singly or in combination.

[0019]

Hydroxy-containing unsaturated compound (c):

The unsaturated group(s) in the compound are unsaturated group(s) that, when irradiated with light, undergoes a radical polymerization reaction and thereby forms a crosslinked structure, and includes known unsaturated groups. Preferable examples include (meth)acryloyl groups.

[0020]

The hydroxy-containing unsaturated compound (c) may be an unsaturated compound (c-1) having one hydroxy group and one unsaturated group per molecule. Examples of the unsaturated compound (c-1) include 2-hydroxyethyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, etc. These can be used singly or in combination.

[0021]

The hydroxy-containing unsaturated compound (c) may be an unsaturated compound (c-2) having one hydroxy group and at least two unsaturated groups per molecule. Examples of the

unsaturated compound (c-2) include glycerol di(meth)acrylate, diglycerol tri(meth)acrylate, trimethylolpropane di(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol penta(meth)acrylate, etc. These can be used singly or in  
5 combination.

[0022]

The hydroxy-containing unsaturated compound (c) may be an unsaturated compound (c-3) having at least two hydroxy groups and one unsaturated group per molecule. Examples of the  
10 unsaturated compound (c-3) include glycerol mono(meth)acrylate, diglycerol mono(meth)acrylate, pentaerythritol mono(meth)acrylate, dipentaerythritol mono(meth)acrylate, dipentaerythritol mono(meth)acrylate, sorbitol mono(meth)acrylate, etc. These can be used singly or in  
15 combination.

[0023]

The hydroxy-containing unsaturated compound (c) may be an unsaturated compound (c-4) having at least two hydroxy groups and at least two unsaturated groups per molecule. Examples of the  
20 unsaturated compound (c-4) include diglycerol di(meth)acrylate, pentaerythritol di(meth)acrylate, dipentaerythritol di(meth)acrylate, dipentaerythritol tri(meth)acrylate, dipentaerythritol tetra(meth)acrylate, sorbitol di(meth)acrylate, sorbitol tri(meth)acrylate, sorbitol tetra(meth)acrylate,  
25 sorbitol penta(meth)acrylate, (meth)acrylic acid adducts of diglycidyl ether compounds (such as (meth)acrylic acid adducts of bisphenol A glycidyl ether, and the like), etc.

[0024]

Polyol (d):

30 A compound having at least two hydroxy groups per molecule can be used as the polyol (d). Examples of the polyol (d) include aliphatic polyols, aromatic polyols, alicyclic polyols and other polyols.

Examples of aliphatic polyols include (poly)methylene  
35 glycol, (poly)ethylene glycol, (poly)propylene glycol, 1,4-

butanediol, 1,3-butanediol, 2,3-butanediol, 1,2-butanediol, 3-methyl-1,2-butanediol, 1,2-pentanediol, 1,5-pentanediol, 1,4-pentanediol, 2,4-pentanediol, 2,3-dimethyltrimethylene glycol, 3-methyl-4,3-pentanediol, 3-methyl-4,5-pentanediol, 2,2,4-trimethyl-1,3-pentanediol, 1,6-hexanediol, 1,5-hexanediol, 1,4-hexanediol, 2,5-hexanediol, 1,4-cyclohexanedimethanol, neopentyl glycol, pentaerythritol, trimethylolpropane, glycerol, etc. Examples of alicyclic polyols include 1,4-cyclohexanedimethanol, tricyclodecanedimethanol, hydrogenated bisphenol A, hydrogenated bisphenol F, bisphenol B, alkylene oxide adducts of hydrogenated bisphenol A, bisphenol B, and hydrogenated bisphenol F, etc. Examples of aromatic polyols include bisphenol A, bisphenol F, bisphenol B, alkylene oxide adducts of bisphenol A, bisphenol B, and bisphenol F, etc. Examples of alkylene oxides include methylene oxide, ethylene oxide, propylene oxide, butylene oxide, etc. The above-mentioned polyols may be used singly or in combination.

Among the above polyols, aromatic polyols are especially preferable since use thereof makes it possible to form a core layer with a high refractive index.

[0025]

The photocurable resin composition for an optical waveguide of the present invention can be produced by known methods for producing conventional polyurethane resins. That is, the carboxy-containing polyol (b) and polyisocyanate compound (a) are first mixed so that isocyanate groups are present in excess (e.g., an isocyanate group/hydroxy group molar ratio of about 2.0 to about 1.1, and preferably about 2.0 to about 1.2), and an addition reaction of isocyanate groups with hydroxy groups is performed to produce a carboxy-containing isocyanate compound. Subsequently, the hydroxy-containing unsaturated compound (c) is added to the carboxy-containing isocyanate compound so that the molar ratio of isocyanate groups to hydroxy groups becomes about 0.8 to about 1.0, and preferably about 0.9 to about 1.0, and an addition reaction was performed. Before the reaction, the carboxy

groups may be blocked by esterification with a lower alcohol such as methanol, ethanol, propanol, or the like; and, after the reaction, carboxy groups can be recovered by removing the lower alcohol by heating.

5 [0026]

When using the polyol (d), the polyol (d), carboxy-containing polyol (b) and polyisocyanate compound (a) are first mixed so that isocyanate groups are present in excess (e.g., an isocyanate group/hydroxy group molar ratio of about 2.0 to about 10 1.1, and preferably about 2.0 to about 1.2), and an addition reaction of isocyanate groups with hydroxy groups is performed to produce a carboxy-containing isocyanate compound. Subsequently, the hydroxy-containing unsaturated compound (c) is added to the carboxy-containing isocyanate compound so that the molar ratio of 15 isocyanate groups to hydroxy groups becomes, for example, about 0.8 to about 1.0, and preferably about 0.9 to about 1.0, and an addition reaction is performed. Before the reaction, the carboxy groups may be blocked by esterification with a lower alcohol such as methanol, ethanol, propanol, or the like; and, after the 20 reaction, carboxy groups can be recovered by removing the lower alcohol by heating.

Alternatively, the carboxy-containing polyol (b), hydroxy-containing unsaturated compound (c) and optionally polyol (d) may be first mixed, followed by a reaction with the 25 polyisocyanate compound (a).

[0027]

In the addition reaction of isocyanate groups with hydroxy groups, for example, the temperature of the reaction system is usually 50 to 150°C, but is preferably not higher than 30 100°C to prevent polymerization of radically polymerizable unsaturated groups. A urethanization catalyst can be used as required. Examples of preferable urethanization catalysts include tin octylate, dibutyltin dilaurate and like organotin compounds. In the production of the polyurethane resin, organic solvents can 35 be used as required. Examples of usable organic solvents include

acetone, methyl ethyl ketone, methyl isobutyl ketone, ethyl acetate, butyl acetate, toluene, xylene, N,N-dimethylformamide, N-methyl-2-pyrrolidone, etc.

[0028]

5           The photocurable resin composition for an optical waveguide of the present invention is a composition that is cured upon irradiation with light. The light means active energy rays, such as electron rays, ultraviolet rays, visible rays, etc. When irradiation with ultraviolet rays or visible rays is performed to  
10 effect crosslinking, photopolymerization initiators and optionally photosensitizers can be added.

[0029]

Known radical photopolymerization initiators can be used, including, for example, benzophenone, benzoin methyl ether,  
15 benzoin isopropyl ether, benzylxanthone, thioxanthone, anthraquinone and like aromatic carbonyl compounds; acetophenone, propiophenone,  $\alpha$ -hydroxyisobutylphenone,  $\alpha,\alpha'$ -dichloro-4-phenoxyacetophenone, 1-hydroxy-1-cyclohexylacetophenone, diacetylacetophenone, acetophenone and like acetophenone  
20 compounds; benzoyl peroxide, t-butylperoxy-2-ethylhexanoate, t-butylhydroperoxide, di-t-butyl diperoxyisophthalate, 3,3',4,4'-tetra(t-butylperoxycarbonyl)benzophenone and like organic peroxides; diphenyliodonium bromide, diphenyliodonium chloride and like diphenylhalonium salts; carbon tetrabromide, chloroform,  
25 iodoform and like organic halides; 3-phenyl-5-isoxazolone, 2,4,6-tris(trichloromethyl)-1,3,5-triazine benzanthrone and like heterocyclic and polycyclic compounds; 2,2'-azo(2,4-dimethylvaleronitrile), 2,2'-azobisisobutyronitril, 1,1'-azobis(cyclohexane-1-carbonitrile), 2,2'-azobis(2-  
30 methylbutyronitrile) and like azo compounds; iron-allene complexes (see European Patent No. 152377); titanocene compounds (see Japanese Unexamined patent Publication No. 1988-221110); bisimidazole compounds; N-aryl glycidyl compounds; acridine compounds; combinations of aromatic ketones and aromatic amines;  
35 peroxyketals (see Japanese Unexamined Patent Publication No.

1994-321895), etc. Among these radical photopolymerization initiators, di-t-butylldiperoxyisophthalate, 3,3',4,4'-tetra(t-butylperoxycarbonyl)benzophenone, iron-allene complexes and titanocene compounds are preferable, since they have high  
5 activity for crosslinking or polymerization.

[0030]

Commercial radical photopolymerization initiators are usable, including, for example, "Irgacure 651" (tradename of Ciba Speciality Chemicals; acetophenone radical photopolymerization  
10 initiator), "Irgacure 184" (tradename of Ciba Speciality Chemicals; acetophenone radical photopolymerization initiator), "Irgacure 1850" (tradename of Ciba Speciality Chemicals; acetophenone radical photopolymerization initiator), "Irgacure  
15 907" (tradename of Ciba Speciality Chemicals; aminoalkylphenone radical photopolymerization initiator), "Irgacure 369" (tradename of Ciba Speciality Chemicals; aminoalkylphenone radical photopolymerization initiator), "Lucirin TPO" (tradename of BASF A.G.; 2,4,6-trimethylbenzoyldiphenylphosphine oxide), "Kayacure  
20 DETXS" (tradename of Nippon Kayaku Co., Ltd.), "CGI-784" (tradename of Ciba Speciality Chemicals; titanium complex compound), etc. These can be used singly or in combination..

Examples of photosensitizing dyes include thioxanthene dyes, xanthene dyes, ketone dyes, thiopyrylium salt dyes, bisstyryl dyes, merocyanine dyes, 3-substituted coumarin dyes,  
25 3,4-substituted coumarin dyes, cyanine dyes, acridine dyes, thiazine dyes, phenothiazine dyes, anthracene dyes, coronene dyes, benzanthracene dyes, perylene dyes, merocyanine dyes, ketocoumarin dyes, fumarine dyes, borate dyes, etc. Such dyes can be used singly or in combination. Examples of borate  
30 photosensitizing dyes include those mentioned in Japanese Unexamined Patent Publications No. 1993-241338, No. 1995-5685 and No. 1995-225474.

[0031]

The photocurable resin composition of the present  
35 invention may contain, where necessary, a polyepoxide.

Examples of usable polyepoxides include bisphenol-type epoxy resins obtained by reacting bisphenols with haloepoxides such as epichlorohydrin,  $\beta$ -methylepichlorohydrin, etc.; halogenated bisphenol-type epoxy resins; phosphorus-modified  
5 bisphenol-type epoxy resins obtained by reaction with phosphorus compounds; alicyclic epoxy resins obtained by hydrogenating bisphenol-type epoxy resins; novolac-type epoxy resins obtained by reacting haloepoxides with phenol novolac resins, cresol novolac resins, etc.; glycidyl ester-type epoxy resins obtained  
10 by reacting epichlorohydrin with polybasic acids such as phthalic acid, dimer acid, etc.; glycidyl amine-type epoxy resins obtained by reacting epichlorohydrin with polyamines such as diaminodiphenylmethane, isocyanuric acid, etc.; linear aliphatic epoxy resins and alicyclic epoxy resins obtained by oxidizing  
15 olefin bonds with peracids such as peracetic acid; biphenyl-type epoxy resins obtained by reacting biphenols with epichlorohydrin; etc.

[0032]

Among such polyepoxides, bisphenol-type epoxy resins,  
20 novolac-type epoxy resins, etc., can be preferably used since they are highly effective for improving heat resistance, which is required of optical waveguides.

[0033]

The photocurable resin composition of the present  
25 invention may contain, if necessary, unsaturated compounds other than those mentioned above; adhesion promoters; hydroquinone, 2,6-di-t-butyl-p-cresol, N,N-diphenyl-p-phenylenediamine and like polymerization inhibitors; saturated resins; unsaturated resins (containing unsaturated groups); fine particles of organic resins  
30 such as vinyl polymers and the like; coloring pigments, extender pigments and like pigments; cobalt oxide and like metal oxides; dibutyl phthalate, dioctyl phthalate, tricresyl phosphate, polyethylene glycol, polypropylene glycol and like plasticizers; anticissing agents; fluidity controlling agents; etc.

35 [0034]

Examples of unsaturated compounds other than those mentioned above include monomers, dimers, trimers and other oligomers that have preferably 1 to 4 radically polymerizable ethylene groups and that, when exposed to light, undergo addition  
5 polymerization to render the exposed portion insoluble. Examples of such compounds include acrylic acid, methacrylic acid, ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, poly(tetra to hexadeca)ethylene glycol di(meth)acrylate, propylene glycol  
10 di(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, ethylene glycol diitaconate, ethylene glycol dimaleate, hydroquinone di(meth)acrylate, resorcinol di(meth)acrylate, pyrogallol (meth)acrylate, oligourethane acrylate, oligoepoxy acrylate, divinylbenzene, etc.  
15 Such ethylenically unsaturated compounds can be used singly or in combination.

[0035]

The amount of ethylenically unsaturated compound to be used is preferably not more than about 200 parts by weight, and  
20 more preferably about 3 to about 50 parts by weight, per 100 parts by weight of carboxy-containing unsaturated polyurethane resin (A).

[0036]

Saturated resins can be used to suppress the solubility  
25 of the photocurable resin (as an agent for suppressing the solubility of the resist film in an alkaline developer or the solubility in, for example, a strongly alkaline developer used for removal of the photocurable film). Examples thereof include polyester resins, alkyd resins, (meth)acrylic resins, vinyl  
30 resins, epoxy resins, phenol resins, natural resins, synthetic rubbers, silicon resins, fluororesins, polyurethane resins, etc. Such resins can be used singly or in combination.

[0037]

Examples of unsaturated resins include the same resins  
35 as mentioned above except for having an average of about 1 to



about 10, and more preferably an average of about 1 to about 4, unsaturated groups per molecule.

[0038]

The amount of saturated resin or unsaturated resin to  
5 be used is preferably not more than about 200 parts by weight, and more preferably about 3 to about 50 parts by weight, per 100 parts by weight of carboxy-containing unsaturated polyurethane resin (A).

The photocurable resin composition of the present  
10 invention may further contain, for example, fillers, coloring agents, leveling agents, heat-resistant stabilizers, discoloration preventing agents, antioxidants, mold releasing agents, surface treating agents, flame retardants, viscosity modifiers, plasticizers, antimicrobial agents, mildew-proofing  
15 agents, antifoaming agents, coupling agents, etc., as required.

[0039]

The photocurable resin composition of the present invention is used as, for example, a liquid resin composition (organic solvent-based or aqueous), or for a dry film resist. It  
20 is particularly preferable to use the photocurable resin composition for a dry film resist.

[0040]

The organic solvent-based liquid resin composition can be prepared by dissolving or dispersing the carboxy-containing  
25 unsaturated polyurethane resin (A) in an organic solvent (a ketone, ester, ether, cellosolve, aromatic hydrocarbon, alcohol, halogenated hydrocarbon, or the like). The composition can be applied on an optical waveguide substrate by roller coating, roll coating, spin coating, curtain roll coating, spray coating,  
30 electrostatic coating, dip coating, silk printing or like method, set as required, and dried to obtain a coating film for an optical waveguide.

[0041]

The aqueous liquid resin composition can be obtained by  
35 dissolving or dispersing the carboxy-containing unsaturated

polyurethane resin (A) in water. The aqueous liquid resin composition can be dissolved or dispersed in water by neutralizing the carboxy group in the carboxy-containing unsaturated resin (A) with an alkali (neutralizer).

5 [0042]

Examples of usable alkaline neutralizers include monoethanolamine, diethanolamine, triethylamine, diethylamine, dimethylaminoethanol, cyclohexylamine, ammonia, etc. The amount of neutralizer is generally 0.2 to 1.0 equivalent, and in particular 0.3 to 0.8 equivalents, per equivalent of carboxy groups.

The dry film can be prepared by applying the aqueous or organic solvent-based liquid resin composition using a roll coater, blade coater, curtain flow coater, or the like, and dried to obtain a coating film for an optical waveguide (dry film thickness of about 1  $\mu$ m to 2 mm, especially preferably 1  $\mu$ m to 1 mm).

[0043]

The dry film thus obtained, after or without peeling off the base film layer, is exposed to visible rays as required so as to form an optical waveguide and then cured; and after peeling off the base film when it has not been peeled off, the cured film can be used for an optical waveguide. When the dry film is formed as a core layer, the dry film can be subjected to development treatment to form a core layer. Where necessary, a cover coat layer can be provided on the dry film. The cover coat layer may be formed by coating or bonded onto the dry film.

The dry film formed using the photocurable resin composition of the present invention preferably has a softening temperature within the range of about 0°C to about 300°C, and more preferably within the range of about 10°C to about 250°C. When the dry film has a softening temperature lower than 0°C, the dry film is softened and becomes sticky when heated for bonding to a substrate, making bonding operation extremely difficult and/or forming bubbles after bonding.

When the dry film has a softening temperature higher than 300°C, the dry film cannot be bonded, making transfer of the dry film impossible.

[0044]

5           As used herein, the softening temperature (TMA) is determined from thermal deformation behavior of a 1 mm-thick resin sheet, using Thermomechanical Analyzer produced by DuPont. Specifically, a load of 49 g is applied to a quartz needle placed on the sheet; the sheet is heated at a rate of 5°C/min; and the  
10   temperature at which the needle penetrates into the sheet to a depth of 0.635 mm is defined as the softening temperature.

[0045]

Light sources usable for photocuring include, for example, extra-high-pressure mercury lamps, high-pressure mercury  
15   lamps, medium-pressure mercury lamps, low-pressure mercury lamps, chemical lamps, carbon arc lamps, xenon lamps, metal halide lamps, tungsten lamps, etc. Various lasers having oscillation lines in the visible region can also be used. In particular, argon lasers having oscillation lines at 488 nm, and YAG-SHG lasers having  
20   oscillation lines at 532 nm are preferable.

[0046]

The optical waveguide of the present invention comprises a lower cladding layer, a core layer, and an upper cladding layer, and at least one of these layers is formed using  
25   the photocurable resin composition or dry film of the present invention.

[0047]

In the present invention, all of the layers may be formed using the photocurable resin composition of the present  
30   invention, or all of the layers may be formed using the photocurable dry film of the present invention. The optical waveguide of the present invention may also be formed by combined use of the resin composition and dry film of the present invention. Further, it is also possible to form the layers  
35   partially using known optical waveguide-forming composition(s)

and/or dry film(s).

[0048]

In the optical waveguide of the present invention, it is preferable that the refractive index difference between the core layer (B) and the lower or upper cladding layer (A) or (C) be at least 0.1%. Specifically, it is preferable that the refractive index of the core layer (B) is greater than that of the lower and upper cladding layers. Thus, it is usually preferable that, for light having a wavelength of 400 to 1,700 nm, the core layer (B) has a refractive index of 1.420 to 1.650, and that each of the lower cladding layer (A) and upper cladding layer (C) has a refractive index of 1.400 to 1.648. The refractive index can be adjusted by suitably selecting the resins, additives, proportions thereof, etc.

[0049]

The refractive index is measured using an Abbe refractometer with light having a wavelength of 589 nm.

In the optical waveguide of the present invention, the thicknesses of the lower cladding layer (A), upper cladding layer (C) and core layer (B) are not limited, and are preferably, for example, each about 1 to about 200  $\mu\text{m}$ . The width of the core layer (B) is not limited, and is preferably about 1 to about 200  $\mu\text{m}$ .

[0050]

Although the process for producing the optical waveguide of the present invention is not limited to the following, the optical waveguide of the present invention can be produced using the photocurable resin composition or dry film of the present invention for forming, in particular, the core layer (B), and using a heretofore known thermosetting resin, radiation-curable dry film, or radiation-curable resin solution for forming the upper or lower cladding layer.

The process for producing the optical waveguide is described below.

[0051]

Lower cladding layer (A)

A known resin such as a thermoplastic resin, curable resin or like resin can be used for the lower cladding layer (A), but it is particularly preferable to form the lower cladding  
5 layer using the curable resin composition or dry film of the present invention.

[0052]

Examples of thermoplastic resins include acrylic resins, epoxy resins, silicon resins, polycarbonate resins,  
10 siloxane resins, polyimide resins, polyurethane resins, oxetane resins, polyethersulfone resins, polyphenyl sulfide resins, polyether imide resins, polysulfone resins, polyether ketone resins, polyamide resins, polyethylene resins, polypropylene resins, polyethylene terephthalate resins, phenol novolac resins,  
15 ethylene-vinyl alcohol copolymers, ethylene-vinyl acetate copolymers, polystyrene resins, fluororesins, polybutylene terephthalate resins, polyacetals resins, polyether nitrile resins, polyamide resins, polyolefin-maleimide copolymers, aramid resins, liquid crystal polymers, polyether ketone resins, cyanate  
20 resins, etc.

[0053]

Examples of curable resins include thermosetting resins, room temperature-curable resins, active energy ray-curable resins, etc. When using an active energy ray-curable  
25 resin, the entire surface of the coating film is irradiated.

[0054]

Usable thermosetting resins include, for example, combinations of base resins having heat-reactive functional groups, and curing agents having functional groups that react  
30 with the heat-reactive functional groups. Also usable are self-crosslinking resins having N-methylol groups, N-alkoxymethylol groups, etc. Examples of combinations of heat-reactive functional groups and functional groups reactive therewith include carboxy groups and epoxy groups (oxirane groups); carboxylic anhydrides  
35 and epoxy groups (oxirane groups); amino groups and epoxy groups

(oxirane groups); carboxy groups and hydroxy groups; carboxylic anhydrides and hydroxy groups; blocked isocyanate groups and hydroxy groups; isocyanate groups and amino groups; etc. In addition, any of the curing systems described in "Kakyo System no  
5 Kaihatsu to Oyo Gijutsu" (Gijutsu Joho Kyokai Shuppan) can be used.

[0055]

Examples of room temperature-curable resins include oxidation-curable unsaturated resins, isocyanate-curable resins,  
10 etc.

[0056]

Known active energy ray-curable resins are resin compositions other than the photocurable resin composition for an optical wavelength according to the present invention, and  
15 include, for example, resins containing, as an essential component, a compound having at least two ring-opening polymerizable functional groups per molecule, optionally in combination with an active energy ray polymerization initiator; resins containing a polymerizable unsaturated compound, an  
20 unsaturated resin, optionally in combination with an active energy ray polymerization initiator; and the like. Also usable are negative-type active energy ray-sensitive resins described hereinafter.

For forming the lower cladding layer (A) using the  
25 above resin, a solution or dispersion of the resin in a solvent such as an organic solvent, water or the like is applied and printed on a substrate, and the solvent is removed to form the lower cladding layer. Further, after or simultaneously with removal of the solvent, the resin may be cured or dried as  
30 required by active energy ray irradiation, heating or like method, to form the lower cladding layer.

[0057]

Alternatively, a solution or dispersion of a known resin composition as mentioned above or the resin composition of  
35 the present invention is applied and printed on a base film, and

the solvent is removed to form a dry film layer on the base film surface. After peeling off the base film, the dry film can be bonded to an optical waveguide substrate by applying heat and pressure to thereby form the lower cladding layer (A). Further  
5 alternatively, a laminate film comprising a dry film layer formed on a base film surface may be bonded to an optical waveguide substrate by applying heat and pressure, followed by removal of the base film, to thereby form the lower cladding layer (A) on a surface of the optical waveguide substrate.

10 [0058]

After bonding the dry film layer bonded to the optical waveguide substrate surface, the resin can be cured or dried by active energy ray irradiation, heating or like method as required, to obtain the lower cladding layer (A).

15 [0059]

From the viewpoint of environmental protection, safety, workability, etc., it is especially preferable to form the lower cladding layer (A) using the dry film.

[0060]

20 From the viewpoint of durability, heat resistance, processability, and optical transmission properties, the resin for forming the lower cladding layer (A) is preferably the resin composition of the present invention or a dry film thereof.

[0061]

25 Core layer (B)

The core (B) is formed on part of the surface of the lower cladding layer (A).

[0062]

The core layer (B) can be formed using a known resin  
30 composition such as a thermoplastic resin, an active energy ray-sensitive resin composition, or the like; but it is especially preferable to form the core layer (B) using the curable resin composition or dry film of the present invention. Examples of known active energy ray-sensitive resin compositions include  
35 those other than the resin composition of the present invention

or dry film thereof, such as known negative-type active energy ray-sensitive resin compositions, positive-type active energy ray-sensitive resin compositions, etc.

Negative-type active energy ray-sensitive resin  
5 compositions are such compositions that when films formed therefrom are cured by irradiation with energy rays such as ultraviolet rays, visible rays, heat rays, etc., the films become insoluble in developers and thereby form core layers. Known such resin compositions can be used without limitation. Specifically,  
10 it is preferable to use, for example, a resin composition comprising as an essential component a compound having at least two ring-opening polymerizable functional groups per molecule, and optionally an active energy ray polymerization initiator; or a resin composition comprising a polymerizable unsaturated  
15 compound, unsaturated resin, and optionally an active energy ray polymerization initiator.

Known positive-type active energy ray-sensitive resin compositions can be used without limitation, as long as films formed therefrom are decomposed when irradiated with energy rays  
20 such as ultraviolet rays, visible rays, heat rays, etc., so as to change the solubility of the irradiated portions of the films in developers and thereby form core layers.

[0063]

Examples of positive-type active energy ray-sensitive  
25 resin compositions include compositions containing, as a main component, a resin in which a quinonediazidesulfonic acid is linked, via a sulfonic ester bond, to a base resin such as an acrylic resin having ion-forming groups (see Japanese Unexamined Patent Publication Nos. 1986-206293, 1995-133449, etc.), i.e.,  
30 naphthoquinonediazide photosensitive compositions that make use of a reaction in which a quinonediazide group is photolyzed by light irradiation to form an indenecarboxylic acid via a ketene; positive-type photosensitive compositions that make use of such a mechanism that when crosslinked films insoluble in alkaline and  
35 acid developers are formed by heating and then irradiated with



light, the crosslinked structure is cleaved by the action of photoacid generators that generate acid groups upon irradiation with light, so that the irradiated portions become soluble in alkaline and acid developers (see Japanese Unexamined Patent  
5 Publication Nos. 1994-295064, 1994-308733, 1994-313134, 1994-313135, 1994-313136, 1995-146552, etc.).

[0064]

Photoacid generators are compounds that generate acid upon exposure to light, and decompose resins by the catalytic  
10 action of the generated acid. Known photoacid generators are usable.

[0065]

Known positive-type heat-sensitive resin compositions are usable, including, for example, positive-type heat-sensitive  
15 compositions containing a heat sensitive resin, ether bond-containing olefinically unsaturated compound and thermoacid generator. Such a composition is disclosed in Japanese Unexamined Patent Publication No. 2000-187326.

[0066]

20 To form the core layer (B), a solution or dispersion of a known resin composition as mentioned above or the resin composition of the present invention is applied and printed on the surface of the lower cladding layer (A), and the solvent is removed to form a resin film that forms the core layer (B). The  
25 solvent is then removed, and the resin film is irradiated with active energy rays to form the core layer (B), and then developed to remove the unirradiated portion when the resin composition of the present invention or a negative-type active energy ray-sensitive resin composition is used, or remove the irradiated  
30 portion when a positive-type active energy ray-sensitive resin composition is used, thereby forming the core layer (B).

[0067]

Alternatively, a solution or dispersion of a known resin composition or the resin composition of the present  
35 invention is applied and printed on a base film, and the solvent

is removed to form a dry film on the base film. The base film is then peeled off, and the dry film is bonded onto the lower cladding layer (A) by applying heat and pressure, thereby laminating the dry film for forming the core layer. Alternatively, 5 the base film may be peeled off after bonding the dry film to the surface of the lower cladding layer (A) by applying heat and pressure. Subsequently, irradiation with active energy rays is performed to form the core layer (B), and then the film is developed to remove the unirradiated portion when a negative-type 10 active energy ray-sensitive resin composition or the resin composition or dry film of the present invention is used, or remove the irradiated portion when a positive-type active energy ray-sensitive resin composition is used, thereby removing the resin film portion other than the portion that forms the core 15 layer (B).

[0068]

Upper cladding layer (C)

The upper cladding layer (C) can be formed on the surfaces of the lower cladding layer (A) and the core layer (B) 20 using a curable resin composition or a dry film.

It is possible to form the upper cladding layer (C) using the photocurable resin composition of the present invention, a dry film thereof, a known thermosetting resin composition or active energy-curable resin as mentioned above, or like resin.

25 The upper cladding layer (C) can be formed in the same manner as for forming the lower cladding layer (A).

Specifically, the upper cladding layer (C) can be formed by applying and printing a solution or dispersion of the photocurable resin composition in an organic solvent, water or 30 like solvent, and removing the solvent. Further, after or simultaneously with removal of the solvent, the resin may be cured or dried by active energy ray irradiation, heating or like method, as required, to form the layer.

[0069]

35 Alternatively, the upper cladding layer (C) can be

formed by applying and printing a solution or dispersion of a resin as mentioned above on a base film, and removing the solvent to form a dry film layer on the base film surface, from which the dry film layer is removed to form the upper cladding layer (C).

- 5 Alternatively, a laminate film comprising a dry film layer formed on a base film surface may be bonded to a substrate, and the base film is peeled off to form the upper cladding layer (C) on the surface of the substrate.

[0070]

- 10 After bonding the dry film layer, the resin be cured or dried by active energy ray irradiation or heating, as required.

[0071]

- Use of a dry film to form the upper cladding layer (C) is preferable from the viewpoint of environmental friendliness, safety, workability, etc.
- 15

[0072]

- It is particularly preferable to form the upper cladding layer (C) using the photocurable resin composition of the present invention or a dry film thereof, from the viewpoint of durability, heat resistance, processability, and optical transmission properties.
- 20

- In the present invention, the upper cladding layer (C) as a dry film before being bonded to the surfaces of the lower cladding layer (A) and core layer (B) preferably has a softening temperature within the range of about 0°C to about 300°C, and more preferably within the range of about 10°C to about 250°C.
- 25

[0073]

- When the dry film has a softening temperature lower than the above, the dry film is softened and becomes sticky when heated for bonding to the substrate, making bonding operation extremely difficult and/or forming bubbles after bonding. When the dry film has a softening temperature higher than the above, bonding the dry film is difficult, making transfer of the dry film impossible.
- 30

- 35 [0074]

The dry film for forming the upper cladding layer (C) preferably has a softening temperature lower than that of the resin layer forming the core layer (B), preferably by 10°C or more.

[0075]

5           Specifically, to form the upper cladding layer (C), the upper cladding layer (C) (dry film) is placed so that the surface thereof comes into contact with the surfaces of the core layer (B) and lower cladding layer (A); suitable heat and pressure are applied to the surface of the base film at a temperature at least  
10 10°C higher than the softening temperature of the dry film, by a pressure-bonding method such as atmospheric-pressure hot roll bonding, vacuum hot roll bonding, vacuum hot press bonding, etc.; and the base film is peeled off from the dry film to transfer the  
15 dry film onto the core layer (B) and lower cladding layer (A); thereby forming an upper cladding layer on the surfaces of the core layer (B) and lower cladding layer (I).

[0076]

After bonding the dry film layer, the resin is cured or dried by active energy ray irradiation or heating to form the  
20 upper cladding layer.

In the present invention, examples of the base film include films of polyethylene terephthalate, aramid, Kapton, polymethylpentene, polyethylene, polypropylene, etc., among which polyethylene terephthalate films are preferable to achieve low  
25 cost and good properties of the dry film. The base film preferably has a thickness of about 1  $\mu\text{m}$  to about 10 mm, and more preferably about 10  $\mu\text{m}$  to about 1 mm.

[0077]

Active energy rays and light rays that can be used in  
30 the present invention include visible rays, ultraviolet rays, infrared rays, x-rays,  $\alpha$ -rays,  $\beta$ -rays,  $\gamma$ -rays, etc. Specifically, for example, it is preferable to use a high-pressure mercury lamp, low-pressure mercury lamp, metal halide lamp, excimer lamp or the like, as an irradiation device. There is no limitation on the  
35 exposure intensity. It is preferable to perform exposure by

irradiation with rays having a wavelength of 200 to 440 nm and an illuminance of 1 to 500 mW/cm<sup>2</sup> at an exposure intensity of 10 to 5,000 mJ/cm<sup>2</sup>.

[Examples]

5 [0078]

The following Examples are provided to illustrate the present invention in further detail, but are not intended to limit the scope of the invention.

Production of photocurable resin composition (1)

10 One hundred grams of photocurable resin obtained by adding 2 mol of trimethylolpropane diacrylate to a reaction product of 1 mol of dimethylolbutanoic acid with 2 mol of tolylene diisocyanate, 3 g of polymerization initiator (tradename "Irgacure 907", product of Ciba Speciality Chemicals) and 400 g  
15 of ethyl acetate were mixed to obtain photocurable resin composition (1).

[0079]

Production of photocurable resin composition (2)

20 One hundred grams of photocurable resin obtained by adding 2 mol of trimethylolpropane diacrylate to a reaction product of 1 mol of dimethylolbutanoic acid, 1 mol of polyethylene glycol (number average molecular weight of 2000), and 3 mol of xylylene diisocyanate, 3 g of polymerization initiator (aminoalkylphenone radical photopolymerization  
25 initiator, tradename "Irgacure 907", product of Ciba Speciality Chemicals) and 400 g of ethyl acetate were mixed to obtain photocurable resin composition (2).

[0080]

Production of photocurable resin composition (3)

30 Forty grams of methyl methacrylate, 40 g of butyl acrylate and 20 g of acrylic acid were subjected to a radical polymerization reaction at 110°C to obtain an acrylic resin solution. Twenty four grams of glycidyl methacrylate, 0.12 g of hydroquinone and 0.6 g of tetraethylammonium bromide were then  
35 added to the solution, and a reaction was carried out at 110°C for

5 hours while introducing air, to thereby obtain a photocurable resin. One hundred grams (solids) of the photocurable resin, 3 g of polymerization initiator (aminoalkylphenone radical photopolymerization initiator, tradename "Irgacure 907", product of Ciba Speciality Chemicals), and 400 g of ethyl acetate were mixed to obtain photocurable resin composition (3).

[0081]

Production of photocurable resin composition (4)

Forty grams of methyl methacrylate, 20 g of styrene, 20 g of butyl acrylate and 20 g of acrylic acid were subjected to a radical reaction at 110°C to obtain an acrylic resin solution. Twenty four grams of glycidyl methacrylate, 0.12 g of hydroquinone and 0.6 g of tetraethylammonium bromide were added to the solution, and a reaction was carried out at 110°C for 5 hours while introducing air, to thereby obtain a photocurable resin. Subsequently, 100 g (solids) of the photocurable resin, 3 g of polymerization initiator (aminoalkylphenone polymerization initiator, tradename "Irgacure 907", product of Ciba Speciality Chemicals) and 400 g of ethyl acetate were mixed to obtain photocurable resin composition (4).

[0082]

Preparation of photocurable dry film D-1

Photocurable resin composition (1) was applied on a polyethylene terephthalate base film (film thickness: 25  $\mu$ m) with a knife edge coater, and dried at 80°C for 30 minutes to obtain photocurable dry film D-1.

[0083]

Preparation of photocurable dry film D-2

Photocurable resin composition (2) was applied on a polyethylene terephthalate base film (film thickness: 25  $\mu$ m) with a knife edge coater, and dried at 80°C for 30 minutes to obtain photocurable dry film D-2.

[0084]

Preparation of photocurable dry film D-3

Photocurable resin composition (3) was applied on a

polyethylene terephthalate base film (film thickness: 25  $\mu$ m) with a knife edge coater, and dried at 80°C for 30 minutes to obtain comparative photocurable dry film D-3.

[0085]

5        Preparation of photocurable dry film D-4

One hundred grams of photocurable resin obtained by adding 2 mol of 2-hydroxyethyl (meth)acrylate to a reaction product of 1 mol of dimethylolbutanoic acid with 2 mol of tolylene diisocyanate, 3 g of polymerization initiator  
10 (aminoalkylphenone radical photopolymerization initiator, tradename "Irgacure 907", product of Ciba Speciality Chemicals) and 400 g of ethyl acetate were mixed to obtain a photocurable resin composition. The composition was applied on a polyethylene terephthalate base film (film thickness: 25  $\mu$ m) with a knife edge  
15 coater, and dried at 80°C for 30 minutes to obtain photocurable dry film D-4.

[0086]

Preparation of photocurable dry film D-5

One hundred grams of photocurable resin obtained by  
20 adding 2 mol of pentaerythritol mono(meth)acrylate to a reaction product of 1 mol of dimethylolbutanoic acid with 2 mol of tolylene diisocyanate, 3 g of polymerization initiator (aminoalkylphenone radical photopolymerization initiator, tradename "Irgacure 907", product of Ciba Speciality Chemicals)  
25 and 400 g of ethyl acetate were mixed to obtain a photocurable resin composition. The composition was applied on a polyethylene terephthalate base film (film thickness: 25  $\mu$ m) with a knife edge coater, and dried at 80°C for 30 minutes to obtain photocurable dry film D-5.

30        [0087]

Preparation of photocurable dry film D-6

One hundred grams of photocurable resin obtained by adding 2 mol of dipentaerythritol di(meth)acrylate to a reaction product of 1 mol of dimethylolbutanoic acid with 2 mol of  
35 tolylene diisocyanate, 3 g of polymerization initiator

(aminoalkylphenone radical photopolymerization initiator, tradename "Irgacure 907", product of Ciba Speciality Chemicals) and 400 g of ethyl acetate were mixed to obtain a photocurable resin composition. The composition was applied on a polyethylene terephthalate film (film thickness: 25  $\mu\text{m}$ ) with a knife edge coater, and dried at 80°C for 30 minutes to obtain photocurable dry film D-6.

[0088]

#### Example 1

#### 10 Production of optical waveguide

##### Formation of lower cladding layer

Photocurable resin composition (3) was applied on a surface of a silicon substrate by spin coating, and irradiated for 100 seconds with ultraviolet rays having a wavelength of 365 nm and an illuminance of 10  $\text{mW}/\text{cm}^2$  to form a lower cladding layer with a thickness of 40  $\mu\text{m}$ .

##### Formation of core layer

Photocurable resin composition (1) was applied on the lower cladding layer by spin coating, and dried at 80°C for 30 minutes. Subsequently, the dry film was then cured by irradiation for 100 seconds with ultraviolet rays having a wavelength of 365 nm and an illuminance of 10  $\text{mW}/\text{cm}^2$ , via a photomask having a pattern consisting of 30  $\mu\text{m}$ -wide lines. The substrate with the ultraviolet ray-irradiated resin composition layer was immersed in a developer made of an aqueous 1.8 wt.% tetramethylammonium hydroxide (TMAH) solution to dissolve the unexposed portion of the resin composition, followed by drying. A core having a pattern consisting of 30  $\mu\text{m}$ -wide lines was thus formed.

##### Formation of upper cladding layer

Photocurable resin composition (3) was applied on the upper surfaces of the core and lower cladding layer on the silicon substrate by spin coating, and irradiated for 100 seconds with ultraviolet rays having a wavelength of 365 nm and an illuminance of 10  $\text{mW}/\text{cm}^2$  to form an upper cladding layer with a thickness of 40  $\mu\text{m}$ .



[0089]

As a result, the transmission loss was rated as A, core gap as A, core shape precision as A, core-covering properties as B, and workability as B.

5 [0090]

Example 2

Production of optical waveguide

Formation of lower cladding layer

10 Photocurable dry film D-3 was transferred onto a surface of a silicon substrate by atmospheric-pressure hot roll bonding (temperature: 100°C), and the polyethylene terephthalate film was peeled off. The dry film was then cured by irradiation for 100 seconds with ultraviolet rays having a wavelength of 365 nm and an illuminance of 10 mW/cm<sup>2</sup> to form a lower cladding layer  
15 with a thickness of 40 μm.

Formation of core layer

Subsequently, photocurable dry film D-1 was transferred onto the lower cladding layer by atmospheric-pressure hot roll bonding (temperature: 100°C), and the polyethylene terephthalate  
20 film was peeled off. The dry film was then cured by irradiation for 100 seconds with ultraviolet rays having a wavelength of 365 nm and an illuminance of 10 mW/cm<sup>2</sup>, via a photomask having a pattern consisting of 30 μm-wide lines. The substrate with the ultraviolet ray-irradiated resin composition layer was immersed  
25 in a developer made of an aqueous 1.8 wt.% tetramethylammonium hydroxide (TMAH) solution to dissolve the unexposed portion of the resin composition, followed by drying. A core layer having a pattern consisting of 30 μm-wide lines was thus formed.

Formation of upper cladding layer

30 Photocurable dry film D-3 was transferred onto the upper surfaces of the lower cladding layer and core by atmospheric-pressure hot roll bonding (temperature: 100°C), and the polyethylene terephthalate film was peeled off. The dry film was then cured by irradiation for 100 seconds with ultraviolet  
35 rays having a wavelength of 365 nm and an illuminance of 10

mW/cm<sup>2</sup> to form an upper cladding layer with a thickness of 40 μm.

[0091]

As a result, the transmission loss was rated as A, core gap as A, core shape precision as A, core-covering properties as  
5 A and workability as A.

[0092]

Example 3

Production of optical waveguide

Formation of lower cladding layer

10 Photocurable resin composition (2) was applied on a surface of a silicon substrate by spin coating, and irradiated for 100 seconds with ultraviolet rays having a wavelength of 365 nm and an illuminance of 10 mW/cm<sup>2</sup> to form a lower cladding layer with a thickness of 40 μm.

15 Formation of core layer

Subsequently, photocurable dry film D-1 was transferred onto the lower cladding layer by atmospheric-pressure hot roll bonding (temperature: 100°C), and the polyethylene terephthalate film was peeled off. The dry film was then cured by irradiation  
20 for 100 seconds with ultraviolet rays having a wavelength of 365 nm and an illuminance of 10 mW/cm<sup>2</sup>, via a photomask having a pattern consisting of 30 μm-wide lines. The substrate with the ultraviolet ray-irradiated resin composition layer was immersed in a developer made of an aqueous 1.8 wt.% tetramethylammonium  
25 hydroxide (TMAH) solution to dissolve the unexposed portion of the coating film, followed by drying. A core layer having a pattern consisting of 30 μm-wide lines was thus formed.

[0093]

Formation of upper cladding layer

30 Photocurable dry film D-2 was transferred onto the upper surfaces of the lower cladding layer and core by atmospheric-pressure hot roll bonding (temperature: 100°C), and the polyethylene terephthalate film was peeled off. The dry film was then cured by irradiation for 100 seconds with ultraviolet  
35 rays having a wavelength of 365 nm and an illuminance of 10

mW/cm<sup>2</sup> to form an upper cladding layer with a thickness of 40 μm.  
[0094]

As a result, the transmission loss was rated as A, core gap as A, core shape precision as A, core-covering properties as  
5 A and workability as B.

[0095]

#### Example 4

##### Production of optical waveguide

##### Formation of lower cladding layer

10 Photocurable dry film D-2 was transferred onto a surface of a silicon substrate by atmospheric-pressure hot roll bonding (temperature: 100°C), and the polyethylene terephthalate film was peeled off. The dry film was then cured by irradiation for 100 seconds with ultraviolet rays having a wavelength of 365  
15 nm and an illuminance of 10 mW/cm<sup>2</sup> to form a lower cladding layer with a thickness of 40 μm.

##### Formation of core layer

Subsequently, photocurable dry film D-1 was transferred onto the lower cladding layer by atmospheric-pressure hot roll  
20 bonding (temperature: 100°C), and the polyethylene terephthalate film was peeled off. The dry film was then cured by irradiation for 100 seconds with ultraviolet rays having a wavelength of 365 nm and an illuminance of 10 mW/cm<sup>2</sup>, via a photomask having a pattern consisting of 30 μm-wide lines. The substrate with the  
25 ultraviolet ray-irradiated resin composition layer was immersed in a developer made of an aqueous 1.8 wt.% tetramethylammonium hydroxide (TMAH) solution to dissolve the unexposed portion of the coating film, followed by drying. A core layer having a pattern consisting of 30 μm-wide lines was thus formed.

##### 30 Formation of upper cladding layer

Photocurable dry film D-2 was transferred onto the upper surfaces of the lower cladding layer and core by atmospheric-pressure hot roll bonding (temperature: 100°C), and the polyethylene terephthalate film was peeled off. The dry film  
35 was then cured by irradiation for 100 seconds with ultraviolet

rays having a wavelength of 365 nm and an illuminance of 10 mW/cm<sup>2</sup> to form an upper cladding layer with a thickness of 40 μm.

[0096]

As a result, the transmission loss was rated as A, core gap as A, core shape precision as A, core-covering properties as A and workability as A.

[0097]

#### Example 5

An optical waveguide was produced in the same manner as in Example 4 except that the core layer was formed using photocurable dry film D-4 in place of photocurable dry film D-1.

[0098]

As a result, the transmission loss was rated as A, core gap as A, core shape precision as A, core-covering properties as A and workability as A.

[0099]

#### Example 6

An optical waveguide was produced in the same manner as in Example 5 except that the core layer was formed using photocurable dry film D-4 in place of photocurable dry film D-1.

[0098]

As a result, the transmission loss was rated as A, core gap as A, core shape precision as A, core-covering properties as A and workability as A.

[0099]

#### Example 6

An optical waveguide was produced in the same manner as in Example 4 except that the core layer was formed using photocurable dry film D-5 in place of photocurable dry film D-1.

[0100]

As a result, the transmission loss was rated as A, core gap as A, core shape precision as A, core-covering properties as A and workability as A.

[0101]

#### Example 7

An optical waveguide was produced in the same manner as in Example 4 except that the core layer was formed using photocurable dry film D-6 in place of photocurable dry film D-1.

[0102]

- 5           As a result, the transmission loss was rated as A, core gap as A, core shape precision as A, core-covering properties as A and workability as A.

[0103]

#### Example 8

#### 10   Production of optical waveguide

##### Formation of lower cladding layer

- A mixture of 100 g (as solids) of photocurable resin composition (3) with 10 g of Epikote EP-828EL (tradename of Japan Epoxy Resin Co., Ltd.) was applied on a surface of a silicon  
15   substrate by spin coating, and irradiated for 100 seconds with ultraviolet rays having a wavelength of 365 nm and an illuminance of 10 mW/cm<sup>2</sup> to form a lower cladding layer with a thickness of 40 μm. The lower cladding layer was then cured by heating at 150°C for 60 minutes.

##### 20   Formation of core layer

- Subsequently, a mixture of 100 g (as solids) of photocurable resin composition (1) with 10 g of Epikote EP-828EL (tradename of Japan Epoxy Resin Co., Ltd.) was applied on the lower cladding layer by spin coating, and dried at 80°C for 30  
25   minutes. Subsequently, the resulting coating was cured by irradiation for 100 seconds with ultraviolet rays having a wavelength of 365 nm and an illuminance of 10 mW/cm<sup>2</sup>, via a photomask having a pattern consisting of 30 μm-wide lines. The substrate with the ultraviolet ray-irradiated resin composition  
30   layer was immersed in a developer made of an aqueous 1.8 wt.% tetramethylammonium hydroxide (TMAH) solution to dissolve the unexposed portion of the resin composition, followed by drying. A core having a pattern consisting of 30 μm-wide lines was thus formed.

##### 35   Formation of upper cladding layer

A mixture of 100 g (as solids) of photocurable resin composition (3) with 10 g of Epikote EP-828EL (tradename of Japan Epoxy Resin Co., Ltd.) was applied on the upper surfaces of the core layer and lower cladding layer by spin coating, and  
5 irradiated for 100 seconds with ultraviolet rays having a wavelength of 365 nm and an illuminance of 10 mW/cm<sup>2</sup> to form an upper cladding layer with a thickness of 40 μm. The upper cladding layer was then cured by heating at 150°C for 60 minutes.

[0104]

10 As a result, the transmission loss was rated as A, core gap as A, core shape precision as A, core-covering properties as B, and workability as B.

[0105]

#### Example 9

#### 15 Production of optical waveguide

##### Formation of lower cladding layer

A photocurable dry film obtained using a mixture of 100 g (as solids) of photocurable resin composition (3) with 10 g of Epikote EP-828EL (tradename of Japan Epoxy Resin Co., Ltd.) was  
20 transferred onto a surface of a silicon substrate by atmospheric-pressure hot roll bonding (temperature: 100°C), and the polyethylene terephthalate film was peeled off. The dry film was then cured by irradiation for 100 seconds with ultraviolet rays having a wavelength of 365 nm and an illuminance of 10 mW/cm<sup>2</sup> to  
25 form an upper cladding layer with a thickness of 40 μm. The lower cladding layer was then cured by heating at 150°C for 60 minutes.

##### Formation of core layer

A photocurable dry film obtained using a mixture of 100 g (as solids) of photocurable resin composition (1) with 10 g of  
30 Epikote EP-828EL (tradename of Japan Epoxy Resin Co., Ltd.) was transferred onto the lower cladding layer by atmospheric-pressure hot roll bonding (temperature: 100°C), and the polyethylene terephthalate film was peeled off. The dry film was then cured by irradiation for 100 seconds with ultraviolet rays having a  
35 wavelength of 365 nm and an illuminance of 10 mW/cm<sup>2</sup>, via a

photomask having a pattern consisting of 30  $\mu\text{m}$ -wide lines. The substrate with the ultraviolet ray-irradiated resin composition layer was immersed in a developer made of an aqueous 1.8 wt.% tetramethylammonium hydroxide (TMAH) solution to dissolve the unexposed portion of the coating film, followed by drying. A core layer having a pattern consisting of 30  $\mu\text{m}$ -wide lines was thus formed. The core layer was then cured by heating at 150°C for 60 minutes.

Formation of upper cladding layer

10           A photocurable dry film obtained using a mixture of 100 g (as solids) of photocurable resin composition (3) with 10 g of Epikote EP-828EL (tradename of Japan Epoxy Resin Co., Ltd.) was applied on the upper surfaces of the core layer and lower cladding layer by atmospheric-pressure hot roll bonding  
15 (temperature: 100°C), and the polyethylene terephthalate film was peeled off. The resulting film was irradiated for 100 seconds with ultraviolet rays having a wavelength of 365 nm and an illuminance of 10  $\text{mW}/\text{cm}^2$  to form an upper cladding layer with a thickness of 40  $\mu\text{m}$ . The upper cladding layer was then cured by  
20 heating at 150°C for 60 minutes.

[0106]

As a result, the transmission loss was rated as A, core gap as A, core shape precision as A, core-covering properties as B, and workability as B.

25           [0107]

Comparative Example 1

Production of optical waveguide

Formation of lower cladding layer

30           Photocurable resin composition (3) was applied on a surface of a silicon substrate by spin coating, and irradiated for 100 seconds with ultraviolet rays having a wavelength of 365 nm and an illuminance of 10  $\text{mW}/\text{cm}^2$  to form a lower cladding layer with a thickness of 40  $\mu\text{m}$ .

Formation of core layer

35           Subsequently, photocurable resin composition (4) was

applied on the lower cladding layer by spin coating, and dried at 80°C for 30 minutes. The resulting film was cured by irradiation for 100 seconds with ultraviolet rays having a wavelength of 365 nm and an illuminance of 10 mW/cm<sup>2</sup>, via a photomask having a pattern consisting of 30 μm-wide lines. The substrate with the ultraviolet ray-irradiated resin composition layer was immersed in a developer made of an aqueous 1.8 wt.% tetramethylammonium hydroxide (TMAH) solution to dissolve the unexposed portion of the resin composition, followed by drying. A core having a pattern consisting of 30 μm-wide lines was thus formed.

#### Formation of upper cladding layer

Photocurable resin composition (3) was applied on the upper surfaces of the core and lower cladding layer on the silicon substrate by spin coating, and irradiated for 100 seconds with ultraviolet rays having a wavelength of 365 nm and an illuminance of 10 mW/cm<sup>2</sup> to form an upper cladding layer with a thickness of 40 μm.

[0108]

As a result, the transmission loss was rated as A, core gap as A, core shape precision as B, core-covering properties as C and workability as B.

Transmission loss: A indicates good transmission properties with a loss of not more than 0.4 dB/cm; and B, poor transmission properties with a loss of more than 0.4 dB/cm.

Light having a wavelength of 850 nm was input to one end of the optical waveguide, and the amount of light output from the other end was measured to determine the transmission loss per unit length using the cut-back method.

Core gap(\*): A indicates that there was no gap between the projecting core and the upper cladding layer; B indicates that there was a gap, or, when an organic solvent-based composition was used, shows that popping and bubbling were generated.

Core shape precision: A indicates that the core layer



was not deformed by the upper cladding layer; and B indicates that the core layer was deformed by the upper cladding layer.

Core-covering properties: A indicates that the thickness of the upper cladding layer at the portion over the projecting core was sufficient; B indicates that the thickness of the upper cladding layer at the portion over the projecting core was slightly small; and C indicates that the thickness of the upper cladding layer at the portion over the projecting core was small.

10 [0109]

Workability: A indicates that the entire process for forming the optical waveguide was simple and easy; B indicates that the entire process was slightly complicated; and C indicates that the entire process was complicated and difficult.

15 [Industrial Applicability]

[0110]

The present invention is applicable as a material for an optical waveguide used for connecting optical fibers to optical devices such as optical integrated circuits, optical modulators, optical switches, optical connectors, optical branching and coupling devices, thin film devices, etc.

[Document Name] Abstract

[Abstract]

[Object] To develop a photocurable resin composition for an optical waveguide.

5 [Means for Achieving the Object]

A photocurable resin composition for an optical waveguide, the composition comprising as an essential component a carboxy-containing unsaturated polyurethane resin (A) obtained by reacting a polyisocyanate compound (a), a carboxy-containing  
10 polyol (b), a hydroxy-containing unsaturated compound (c), and optionally a polyol (d); the polyisocyanate compound (a) being a polyisocyanate compound containing an aromatic ring in its molecule; the hydroxy-containing unsaturated compound (c) being an unsaturated compound (c-1) having one hydroxy group and one  
15 unsaturated group per molecule, an unsaturated compound (c-2) having one hydroxy group and at least two unsaturated groups per molecule, an unsaturated compound (c-3) having at least two hydroxy groups and one unsaturated group per molecule, or an unsaturated compound (c-4) having at least two hydroxy groups and  
20 at least two unsaturated groups per molecule.

[Selected Figure] None